Humidity effect on tribochemical removal of GaAs surface

Bingjun Yu[1,2], Jian Gao[1], Chenning Jin[1], Chen Xiao[1], Jiang Wu[2], Huiyun Liu[2], Shulan Jiang[1], Lei Chen[1], and Linmao Qian[1]*

[1]*Tribology Research Institute, National Traction Power Laboratory, Southwest Jiaotong University, Chengdu 610031, Sichuan Province, P.R. China*

[2]*Department of Electronic & Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK*

E-mail: linmao@swjtu.edu.cn

The defect-free tribochemical removal of gallium arsenide (GaAs) was demonstrated in vacuum, dry air and various humidity by scratching with a SiO_2 tip. The removal depth increases with the relative humidity (1%-90%), and reaches to its maximum value in water. The perfect crystal matrix without defects was observed on the cross section of the scratched groove by a transmission electron microscope. A model based on the reactive tip scratching-induced oxidation, water-solubility of debris and adhesion effect was proposed to interpret the tribochemical removal of GaAs surface. This study provides a new insight into the defect-free and site-controlled nanofabrication on GaAs.

Gallium arsenide (GaAs) serves as an excellent host for optoelectronic devices, because of its excellent physical properties such as direct bandgap and high electron mobility.[1,2] It is one of substrates for new generation of quantum structures for solar cells and laser devices.[3,4] Especially, patterned GaAs substrate provides an effective way for forming nanoscale structures and upgrading the performance of optoelectronics devices.[5,6] However, the defects such as dislocations can be introduced during patterning substrates, and will degrade the optical properties.[7,8] For improving the performance of GaAs-based device, it is of great significance to fabricate patterned GaAs substrates without introducing crystal defect.[9] How to realize the defect-free patterns on GaAs substrate remains an issue for the fabrication of high-performance device.

Recently, tribochemical removal by reactive tip scratching on GaAs surface provides an effective method to produce defect-free substrate with nanoscale holes and grooves.[10,11] Different from the plastic deformation induced by mechanical cutting with a diamond tip,[12,13] the material removal can be realized on GaAs surface by a SiO_2 tip with the contact pressure less than the yield pressure of GaAs. However, the mechanism for the tribochemical removal on GaAs is still far from clear understanding. For the tribochemical reaction of SiO_2/Si pair, the adsorbed water on silicon surface was found to play a key role in the tribochemical removal of silicon surface.[14] It is of motivation to investigate the humidity-dependent material removal on GaAs, which may provide new insight into the understanding of the tribochemical process and facilitates the site-controlled nanofabrication.

In the present study, nanoscratching with a SiO_2 tip was performed on n-type GaAs(100) surface in vacuum, water and humid air with the humidity ranging from 1%-90%, respectively. Before the nanoscratch tests, GaAs wafers were ultrasonically washed in acetone, alcohol and deionized water for 3 min in turn, to remove the surface contaminations, and then were dried by pure nitrogen gas. By an AFM (E-sweep, Hitachi, Japan), the surface root-mean-square (RMS) roughness of GaAs surface was measured as less than 0.5 nm over a 2 μm × 2 μm area. A SiO_2 tip (Novascan Technologies, USA) with a tip radius R of 1.25 μm was used for the nanoscratch test. The relative humidity RH ranging from 1% to 90% was controlled by adjusting the ratio of H_2O vapor and dry air in AFM chamber.[15] For the scratching, the applied normal load F_n was 2 μN, the sliding velocity v was set as 10 μm/s, and the number of scratching cycles N was 100 (one cycle included a reciprocate scratching). For comparison, the scratching was also performed in vacuum (~1 Pa) and in deionized water under the same loading conditions. The

topographies of the scratched surface were scanned by a Si_3N_4 tip with R≈20 nm (MSCT, Bruker Corporation, USA) in vacuum. In addition to a SiO_2 tip (R=600 nm), a diamond tip (R=600 nm; Micro Star Technologies, USA) was also used for the test of adhesive force F_a. All AFM tests were conducted under a temperature of about 25 ^oC.

To study the wear of the SiO_2 tip, a probe grating (TGT1, NT-MDT Co., Russia) was used to detect the tip topography before and after the scratch tests under N=2000, F_n=2 μN and RH=50%. The cross-section microstructure of the scratched area after material removal under RH=50% and F_n=2 μN was observed by a transmission electron microscope (TEM; FEG Philips Tecnai F20, FEI, The Netherlands). The TEM cross-section sample was prepared by the focused ion beam (FIB) after depositing polymer and platinum layer in turn onto the target area.

Fig. 1 shows the AFM images of the scratches on GaAs after material removing by SiO_2-tip scratching. When the scratch tests were performed in humid air, the relative humidity (1%-90%) had a strong effect on the material removal of GaAs surface. The removal of material becomes more and more obvious with the increase in relative humidity. For comparison, the scratch tests were repeated in vacuum and in water under the same loading conditions, respectively. Shallower scratches were produced either in vacuum or in dry air, while much deeper grooves were produced in water.

The variation of the groove depth and width is plotted as a function of the humidity as shown in Fig. 2. When RH is 1%, the scratch depth is about 1.4 nm, which is a little deeper than that produced in vacuum (0.5 nm). The groove width undergoes a similar trend as the depth (Fig. 2). The variation could be understood in terms of that the oxygen and absorbed water under such low vacuum or low humidity will promote the oxidation and removal of surface material,[16] and higher content of oxygen and water can facilitate the tribochemical process. The material removal gets much more obvious when the wet air is introduced into the chamber. The depth reaches 3.2 nm at RH=10% and 8.5 nm at RH=90%. When the test is performed in water under the same loading condition, the depth reaches its maximum value of 19.6 nm. These results clearly indicate that the existence of water has a great impact on the material removal on GaAs. Here, it should be noted that the applied load used for the scratching by the SiO_2 tip was 2 μN, corresponding to the Hertzian contact pressure of 0.8 GPa, which is much less than the yield pressure of 4.9 GPa.[17] The material removal thus mainly results from tribochemical reaction.[11]

For mechanical scratching on GaAs surface, severe plastic deformation, including lattice bending, crack, dislocation and stacking, could be found beneath the scratches by TEM

study.[12,13,18] Such defects were caused by the fierce plough of the tip, where the contact pressure can lead to the yield of GaAs substrate. Here, tribochemical removal is realized in a lower contact pressure in the present study. Consequently, the peeling of surface material could undergo a different mechanism. To understand the mechanism of tribochemical removal, the cross section of the groove on GaAs after material removal by the SiO_2 tip was investigated by the TEM, and the result was shown in Fig. 3. A perfect crystal matrix without any defect was observed from the cross-section microstructure of the groove bottom. This suggests that SiO_2-tip scratching can lead to defect-free material removal on GaAs surface without damage to the remaining substrate.

To study the wear of the SiO_2 tip, the topography of the tip before and after the scratch tests was scanned by a sharp tip grating on the AFM. As illustrated in Fig. 4, no obvious change of the tip shape (micro spherical crown) can be detected from the AFM images and profiles. It should be noted that the formation of some debris on the top of the tip after the test is at random, and even can be hardly detected on another SiO_2 tip after scratching on GaAs. Since no cracks and peeling can be found on the tip after scratching, the debris must come from GaAs surface during scratching.

Considering that the contact pressure in this study is much lower than the yield pressure of GaAs (4.9 GPa; see section 3.1), the material removal must be dominated by chemical reaction rather than plastic deformation. In contrast, when the GaAs was scratched by a diamond tip under the contact pressure below 4.9 GPa, groove can be hardly created.[10] It is reasonable to deduce that there is some difference between the interfaces of SiO_2 tip/GaAs and diamond tip/GaAs. To verify this, the adhensive force F_a was measured and shown in Fig. 5. For the SiO_2 tip/GaAs pair, F_a increased with the humidity, while dropped to about 11 nN in water (Fig. 5(a) and Fig. 5(c)). It is suggested that the capillary condensation can be responsible for the humidity-dependent variation of adhensive force.[19] When the test system is immersed in water, the water capillary on the interface disappears, and adhensive force is expected to drop down. In contrast, the adhensive force measured from the diamond tip/GaAs pair under various conditions is quite small and hard to be detected (Fig. 5(b)). For the tribochemical test in the nanoscale, a SiO_2 tip demonstrates higher chemical reactivity than that of a diamond tip.[14] Therefore, it can be deduced that the combination of water meniscus and chemical reactivity contributes mainly to the adhensive force, rsulting in a higher adhensive force for the SiO_2 tip/GaAs system. As a result, since the adhensive force measured from SiO_2/GaAs pair is larger than that from diamond/GaAs pair under the same test condition, GaAs surface with native

oxide layer is opt to be absorbed by the SiO_2 tip.

It is well known that there are two necessary conditions for the friction-induced tribochemical removal on monocrystalline silicon surface.[14] The adsorbed water on silicon surface facilitates the hydrolysis and activation of interface during scratching. On the other hand, a chemically reactive tip, i.e. SiO_2 tip, can result in the formation of interfacial bonds, which will eventually pull the material away from the scratched area. Therefore, a possible mechanism is that the tribochemical removal on GaAs depends on the dynamic formation and break of the interfacial Ga(As)-O-Si bonds, where the Ga-As bond has relatively lower bonding energy and can be easier stretched and broken by scratching.[10,11] However, it remains unknown how the debris is removed in the sliding process.

In the nanoscratching test, the oxidation induced by sliding plays a very important role in the tribochemistry-induced removal of materials.[20] Based on the XPS detection, oxides-rich debris was found from the frictional system of SiO_2/GaAs.[10] Taking into account the humidity-dependent removal, intact ball with debris and the perfect matrix in the GaAs substrate, a new insight into the tribochemical removal on GaAs during scratching can be understood as the schematic diagram in Fig. 6. Firstly, tip scratching facilitates the oxidation of GaAs in the interface of SiO_2/GaAs pair with the existence of (adsorbed) water and oxygen. The adsorbed water and oxygen play key roles in the oxidation of GaAs surface,[10,16] and the scratching can accelerate the oxidation process. Although any kind of tip material can lead to the oxidation in the contact area, a chemically active material, such as SiO_2, is expected to excite easily the molecules in scratched area and enable more mediums to react chemically with the contact area.[14,19,20] The chemically active tip can be viewed as the one that has the trend to be chemically bonded to its counterpart or can be easily physically adhered to the counterpart. Secondly, the adhesion between the tip and scratched area (with oxides) brings the oxides out of the scratch. The arsenic oxides debris is water-soluble and can hence adsorb the surface water.[21] The water-solubility of arsenic oxides can lead to the softening of the debris and promote greatly the removal of debris during tip sliding. During the sliding, the debris is physically adsorbed onto the tip, and dumped during the turning of the tip at the end of the line scratch. Higher humidity is expected to cause more debris dissolution and deeper groove formation. Moreover, larger adhesion facilitates the pull and push of oxide debris during sliding. In the present study, the adhesion force measured on GaAs surface by the SiO_2 tip is larger than that by the diamond tip (Fig. 5), and SiO_2 tip-scratching can thus lead to obvious materials removal. Due to the formation and dissolution of debris, the

interfacial Ga(As)-O-Si bonds are expected to dynamically form and break at the side of GaAs.[10] Thirdly, tip scratching-induced oxidation of GaAs surface continues during the process. In the meantime, the groove gets deeper as the new oxides of $Ga(As)O_x$ are tided away.

Upon above process, scratching under low pressure can accelerate the oxidation under humid condition and lead to no mechanical damage to the GaAs substrate. For the test in water, the water can facilitate the formation of oxidation debris induced by the scratching. Although the adhesive force is very low (~11 nN), the arsenic oxides debris can be completely dissolved by enough water, which can promote greatly the removal of debris during tip sliding.[21] In contrast, slight material removal in low humidity of 1% can be mainly ascribed to the limitation of oxidization. The groove produced in vacuum has the shallowest depth in the present study, which can be mainly ascribed to the extremely limited water and oxygen in vacuum. Since the removal depth increases with the humidity and attains to its maximum in water, the contribution of the water to the chemical reaction is deduced to be more than that of the oxygen. In addition, although the dynamic formation and break of the interfacial chemical bonds can play roles in the sliding process,[10,11] the proposed mechanism in this study is believed to dominate the tribochemical removal of GaAs.

Summarily, the defect-free tribochemical removal of GaAs was realized under vacuum, dry air and various humidity by scratching with a SiO_2 tip. The removal depth increases with the humidity (1%-90%), and reaches its maximum value in water. No obvious damage was observed on the SiO_2 tip before and after the wear test. Perfect crystal matrix was found on the cross section of the scratched groove on GaAs by TEM. Following the results, a model involving the reactive tip scratching-induced oxidation, water-solubility of debris and adhesion effect was proposed for interpreting the tribochemical removal process on GaAs. This study provides a new opportunity towards the defect-free and site-controlled nanofabrication based on the AFM. The SiO_2 tip is proved to be intact after scratching, and a controllable fabrication of surface grooves can be realized on GaAs surface under a given scratching condition. With the help of multiple-probe technology,[22] the tribochemical removal points out a new route to produce patterned GaAs substrate for the fabrication of site-controlled quantum dots and nanowires for high-quality devices.[23,24]

Acknowledgments

The authors are grateful for the support by the Natural Science Foundation of China

(51305365, 51527901 and 91323302), and the Fundamental Research Funds for the Central Universities (2682015CX037).

References

1) A. E. Almand-Hunter, H. Li, S. T. Cundiff, M. Mootz, M. Kira, and S. W. Koch, Nature **506**, 471 (2014).
2) J. Yoon, S. Jo, I. S. Chun, I. Jung, H. S. Kim, M. Meitl, E. Menard, X. Li, J. J. Coleman, U. Paik, and J. A. Rogers, Nature **465**, 329 (2010).
3) P. Krogstrup, H. I. Jørgensen, M. Heiss, O. Demichel, J. V. Holm, M. Aagesen, J. Nygard, and A. F. i Morral, Nat. Photonics **7**, 306 (2013).
4) E. U. Rafailov, M. A. Cataluna, and W. Sibbett, Nat. Photonics **1**, 395 (2007).
5) R. Leon, S. Chaparro, S. R. Johnson, C. Navarro, X. Jin, Y. H. Zhang, J. Siegert, S. Marcinkevičius, X. Z. Liao, and J. Zou, J. Appl. Phys. **91**, 5826 (2002)
6) H. B. Lan and Y. C. Ding, Nano Today **7**, 94 (2012).
7) S. M. Willis, J. A. R. Dimmock, F. Tutu, H. Y. Liu, M. G. Peinado, H. E. Assender, A. A. R. Watt, and I. R. Sellers, Sol. Energ. Mat. Sol. C. **102**, 142 (2012).
8) H. Y. Liu, T. Wang, Q. Jiang, R. Hogg, F. Tutu, F. Pozzi, and A. Seeds, Nat. Photonics **5**, 416 (2011).
9) Y. Y. Zhang, J. Wu, M. Aagesen, and H. Y. Liu, Phys. D: Appl. Phys. **48**, 463001 (2015).
10) C. F. Song, X. Y. Li, H. S. Dong, B. Y. Yu, Z. M. Wang, and L. M. Qian, Sci. Rep. **5**, 9020 (2015).
11) B. Y. Yu, J. Gao, L. Chen, and L. M. Qian, Wear **330–331**, 59 (2015).
12) K. Wasmer, M. Parlinska-Wojtan, S. Graça, and J. Michler, Mater. Chem. Phys. **138**, 38 (2013).
13) M. P. Wojtan, K. Wasmer, J. Tharian, and J. Michler, Scripta Mater. **59**, 364 (2008).
14) J. X. Yu, S. H. Kim, B. J. Yu, L. M. Qian, and Z. R. Zhou, ACS Appl. Mater. Interfaces 4, 1585 (2012).
15) L. Chen, Y. J. Yang, H. T. He, S. H. Kim, and L. M. Qian, Wear **332–333**, 879 (2015).
16) J. F. Bauters, R. E. Fenlon, C. S. Seibert, W. Yuan, J. S. B. Plunkett, J. Li, and D. C. Hall, Appl. Phys. Lett. **99**, 142111 (2011).
17) P. Tang, B. J. Yu, J. Guo, C. F. Song, and L. M. Qian, Nanoscale Res. Lett. **9**, 59 (2014).
18) Y. Q. Wu, H. Huang, and J. Zou, Mater. Lett. **80**, 187 (2012).
19) X. D. Xiao, and L. M. Qian, Langmuir **16**, 8153 (2000).
20) J. Guo, B. J. Yu, L. Chen, and L. M. Qian, Sci. Rep. **5**, 16472 (2015).
21) M. Beerbom, Th. Mayer, and W. Jaegermann, J. Phys. Chem. B **104**, 8503 (2000).
22) Z. J. Wu, C. F. Song, J. Guo, B. J. Yu, and L. M. Qian, Front. Mech. Eng. **8**, 333 (2013).

23) J. Herranz, L. Wewior, B. Alén, D. Fuster, L. González, and Y. González, Nanotechnology 26, **195301** (2015).

24) A. P. Foster, J. P. Bradley, K. Gardner, A. B. Krysa, B. Royall, M. S. Skolnick, and L. R. Wilson, Nano Lett. **15**, 1559 (2015).

Figure Captions

Fig. 1. AFM images (top) and the corresponding profiles (bottom) of the scratches on GaAs surface scratched by the SiO_2 tip in vacuum, water and various relative humidity.

Fig. 2. Variation of the groove depth and width as a function of relative humidity

Fig. 3. TEM image of the cross-section microstructure of the groove on GaAs created under RH=50% and F_n=2 μN. The left figure shows schematically the place where the cross-section sample was obtained.

Fig. 4. AFM images of the SiO_2 tip (a) before and (b) after the scratch tests, and (c) the comparison of the corresponding profiles. The dotted lines in (a) and (b) show the place where the profile is taken.

Fig. 5. The adhensive force F_a measured on GaAs surface by a SiO_2 tip (R=600 nm) and by a diamond tip (R=600 nm), respectively. Under RH=50%, (a) F_a of about 120 nN is measured by the SiO_2 tip, while (b) F_a measured by the diamond tip is too low and submerged in the noise peaks. (c) F_a measured by the SiO_2 tip under vacuum, water and various humidity.

Fig. 6. The process for tribochemical removal on GaAs surface during scratching. (a) Schematic model. (b) AFM image of the scratched GaAs surface with debris without washing.

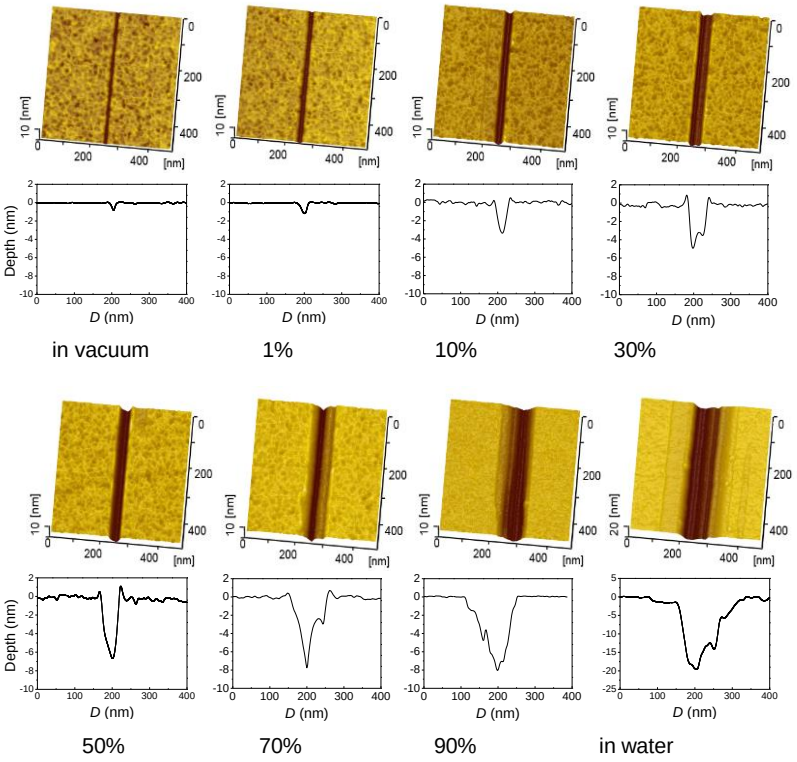

Fig.1.

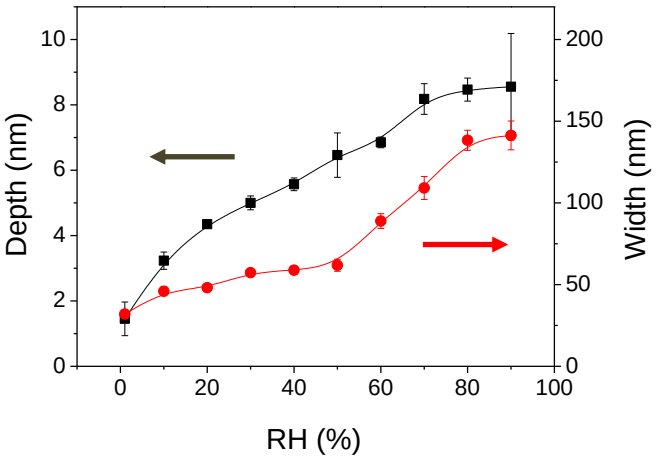

Fig. 2.

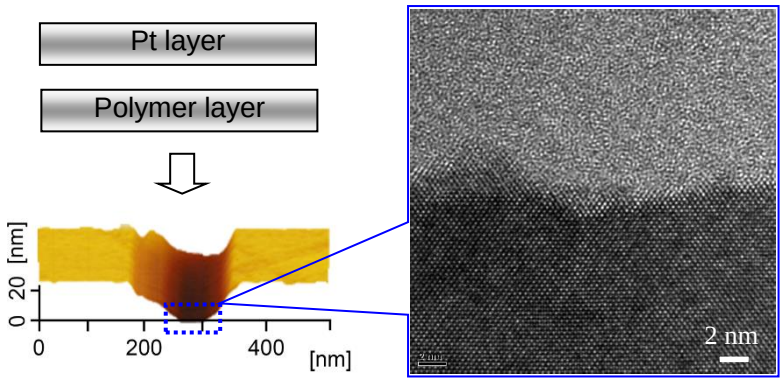

Fig. 3.

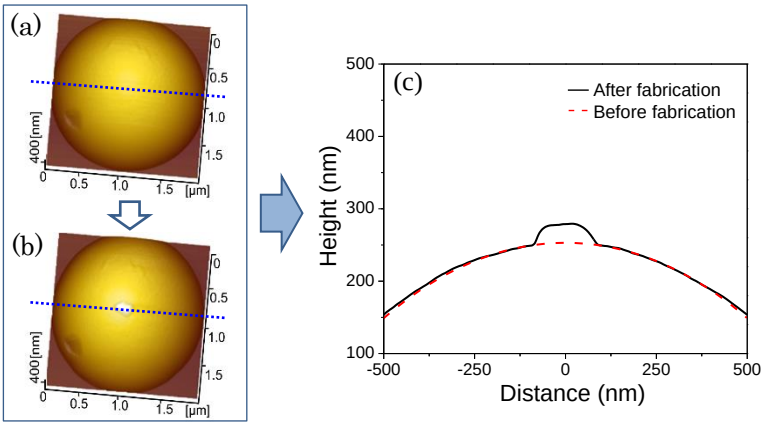
(a)
(b)
400[nm]
0
0.5
1.0
1.5
[μm]
(c)
After fabrication
Before fabrication
Height (nm)
Distance (nm)
500
400
300
200
100
-500
-250
0
250
500

Fig. 4.

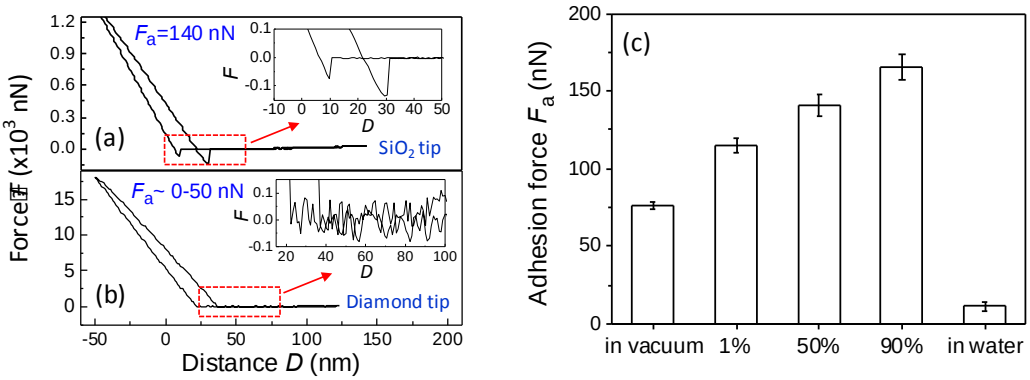
Force F (x10^3 nN)
Distance D (nm)
(a)
F_a=140 nN
SiO2 tip
(b)
F_a~ 0-50 nN
Diamond tip
F
D
(c)
Adhesion force F_a (nN)
in vacuum
1%
50%
90%
in water

Fig. 5.

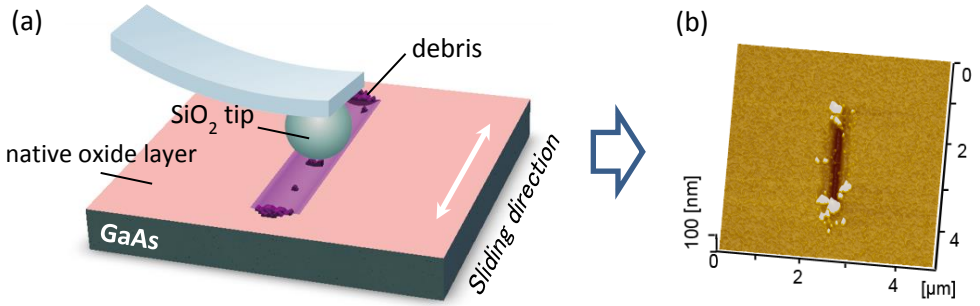

Fig. 6.

Released January 2014